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A promising approach to co-processing calcium-rich coal and an aqueous condensate from biomass carbonization

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HIGHLIGHTS

- A new approach is proposed for co-processing calcium-rich coal with aqueous condensate (AQ).
- The organic contaminants in the AQ were mostly adsorbed onto coal particles during the blending operation.
- Synergy effect in co-gasification and combustion reactivity of DL/AQ blend was observed.
- The AQ enables crystalline calcium species to be highly dispersed on the surface of the coal as in-situ catalyst.

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ABSTRACT

The pretreatment of biomass via torrefaction and low-temperature carbonization produces a high-quality biochar that is more favorable to co-gasification and/or co-combustion with coal. However, the production of biochar is the consequence of dehydration and devolatilization reactions that result in the simultaneous formation of an aqueous condensate (AQ) containing small amounts of organic contaminants. The arbitrary discharge of such a wastewater fraction would cause serious environmental pollution. In this paper, we specifically address this issue. A potential approach has been proposed for the disposal of AQ in combination with gasification (or combustion) of calcium-rich coals. During the operation of blending coal and AQ, most of the organic contaminants in AQ can be physically or chemically adsorbed onto the surface of coal and can thereby be co-gasified or co-combusted together with coal. The most attractive technical benefit of the proposed approach is that such a combination has synergistic effects during co-gasification and co-combustion of the binary mixtures of calcium-rich coal and the AQ. The same effects can also be achieved using a calcium-deficient coal by co-processing it with an AQ solution containing dissolved shell wastes. In addition, both the indigenous crystalline calcite minerals in coal and the dissolved shell wastes show good desulfurization performance during combustion.

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1. Introduction

Over the past few decades, the huge consumption of coal has caused a serious global energy crisis and environmental pollution. Coal emits various contaminating substances, including NO_x, SO_x and CO_2, during its conversion or utilization processes [1]. Biomass is a renewable and clean energy source because of its replenishment, carbon neutrality, and low sulfur content; it is therefore environmentally friendly when utilized for energy production. However, biomass is also a widely dispersed, bulky, and low-energy-density fuel, which leads to some drawbacks: biomass is cost-prohibitive to collect and transport, its supply is insufficient for an economical plant size due to seasonal variations, and biomass-based conversion technologies provide relatively poor performance with high operating costs [2].

A very promising approach to mitigating the aforementioned drawbacks is to co-process coal and biomass in existing coal-based systems. For example, biomass can be co-fired in coal-fired boilers or co-gasified in coal-fired gasifiers [3–5]. These co-processing systems can provide both environmental and economic benefits, including lower emissions of SO_x, NO_x and CO_2 than coal-fired power plants, and economies of scale that can reduce specific operating costs to allow better use of biomass than would be the case in conventional biomass conversion processes [6].

Biomass can be either directly or indirectly co-processed with coal. In the case of a direct co-combustion or co-gasification system equipped with pulverized coal boiler or gasifier, biomass is firstly fed together with coal into a hammer mill and then be fed together into the boiler or gasifier [7]. In principle, this approach is the

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simplest option and involves the smallest financial investments. However, the fibrous structure of fresh biomass makes it less friable and less grindable than coal [8]. This fact implies that biomass particles may always be much larger than coal particles, which negatively affects blend-fuel transport properties and therefore limits the blending percentage of biomass to 5–10 wt% [7]. A method for pre-modifying biomass prior to combustion or gasification to allow homogenization of the different biomass feedstocks into a coal-like biofuel to accommodate existing coal-fired boilers or gasifiers is needed.

Torrefaction and low-temperature carbonization are slow pyrolysis processes for thermally pre-treating biomass at temperatures from 200 to 500 °C in the absence of oxygen or in a low-oxygen environment for several minutes to several hours [9–11]. This treatment can improve the properties of biomass and therefore offers some solutions to the previously mentioned problems. After torrefaction and carbonization, the fibrous structure of biomass is partially or entirely broken down. The weakened fibrous structure improves the grindability of the torrefied or carbonized biomass and enables biomass to be processed together with coal [12,13]. Typical mass-balance analyses for torrefaction and carbonization of the different biomass feedstocks have indicated that 50–70% of the mass is retained as carbon-rich solid products [14]. The other 30–50% of the mass is converted into condensable liquids (mostly water, acetic acid, and other oxygenates) and non-condensable gases (mainly CO_2, CO, and small amounts of methane). Although torrefaction or carbonization processes can transfer a substantial amount of the chemical energy from the feedstock to the solid biochar, it simultaneously and inevitably produces an aqueous condensate (AQ) fraction that contains small amounts of oxygenated organics. Obviously, an AQ contains the majority of the low-quality volatiles in biomass, and some light tar and phenolic derivatives in it are harmful to the environment and to human health, even at low concentrations, because of their toxicity and carcinogenic properties [15]. The disposal of the AQ using traditional wastewater treatment technologies is energy intensive and costly, which greatly diminishes the technical benefits of upgrading biomass via a carbonization pretreatment. Therefore, a technically and economically feasible approach to the disposal of the AQ fraction should be developed. To date, little attention has been devoted to this subject [16].

This work aims to explore a co-processing solution in which the AQ fraction can be simultaneously disposed during the gasification or combustion of calcium-rich coal. Attention is focused on the following subjects: (1) verification of the positive effect of a carbonization pretreatment on upgrading biomass into a commodity fuel through product characterization; (2) examination of the synergistic effects of the combination of calcium-rich coal and AQ during gasification and combustion; and (3) evaluation of the self-desulfurization performance of both the indigenous crystalline calcite minerals in coal and the dissolved shell wastes during combustion.

2. Material and methods

2.1. Materials

Two Chinese bituminous coals, Daliuta (DL) and Datong (DT), were used as the starting materials. DL is a calcium-rich coal, whereas DT is a calcium-deficient coal. The coal samples were pulverized to a particle size less than 75 μm and dried at 105 °C before use.

The biomass samples used in this study included walnut shells (WS) and bamboo sawdust (BS). The raw WS was broken into pieces of 5–10 mm. The particle sizes of BS were less than 2 mm, and this material was used as received. The proximate and ultimate analyses of coal and biomass samples are shown in Table 1.

Manila clam shell (MS) from seafood wastes was pulverized into a fine powder and used as a calcium additive.

2.2. Biomass carbonization and product analyses

Biomass carbonization was conducted in a down-flow laboratory-scale fixed-bed reactor. The reactor comprised an electric heater and a quartz reaction tube with an i.d. of 60 mm. Briefly, 20–30 g of biomass sample was previously packed into the quartz tube. For each run, the quartz tube was heated at 15 °C/min to 350 °C and maintained at this temperature for 20 min under a nitrogen flow of 100 mL/min. The liquid collection unit was composed of a round-bottom flask warmed in an oil bath at 110 °C and a trap cooled by tap water. The round-bottom flask was used to collect a heavy condensable oil (HCO) fraction, and the trap was used to cool exhaust gas to collect an AQ fraction with a boiling point less than 110 °C.

The water content of the AQ was measured by Karl Fischer titration, and its acidity was measured directly using a pH meter. The chemical composition of the AQ was characterized by gas chromatography–mass spectrometry. The density of all the liquid products was determined by measuring the mass of 1 mL volume of liquid (micropipette sampling) at room temperature.

2.3. Sample blending and co-processing

DL coal was used to investigate the effect of the DL to AQ blending ratio on the reactivities of char gasification and combustion. A 0.5 g sample of raw DL coal was placed in a ceramic crucible and blended with AQ in different ratios. The sample prepared in this way, hereafter referred to as the AQ-blended DL coal, was denoted as DL/AQ. The raw coal and AQ-blended samples were dried at 105 °C for 2 h. For char preparation, a set of sample-filled crucibles was simultaneously placed in a muffle furnace preheated to 850 °C and was soaked for 5 min. The crucibles were removed from the furnace and allowed to cool to ambient temperature. During the aforementioned procedure, a lid was always placed on each crucible.

The gasification or combustion reactivity of the previously prepared chars was determined by thermogravimetric analysis in CO_2 at 850 °C or in air at 800 °C under isothermal conditions. Approximately 5 mg of the char sample was placed in an alumina pan and heated at a heating rate of 15 °C/min to the desired temperature under a continuous argon flow of 200 mL/min. The isothermal

Table 1
Properties of coal, biomass and its typical products obtained via carbonization at 350 °C.

	Coal		Biomass		Biochar		HCO[a]
	DL	DT	WS	BS	WS-350	BS-350	BS-HCO
Proximate analysis (wt%, db)							
Volatile matter	35.3	31.9	78.1	81.5	24.6	20.6	88.3
Fixed carbon	58.4	57.2	19.3	16.6	68.1	74.3	11.6
Ash	6.3	10.9	2.6	1.9	7.3	5.1	0.1
HHV[b] (MJ/kg, db)	29.9	30.0	19.7	18.4	28.1	27.7	22.3
Ultimate analysis (wt%, db)							
C	75.8	75.1	51.1	49.4	73.8	74.8	54.9
H	4.5	4.3	6.9	6.1	4.6	3.7	7.3
N	0.9	0.7	0.3	0.3	1.2	0.4	0.6
S	0.2	0.8	0.2	0.1	0.2	0.2	0.1
O[c]	12.3	8.2	41.5	44.1	18.9	16.0	37.1

[a] Heavy condensable oil.
[b] Higher heating value.
[c] By difference.

gasification or combustion of the char was initiated by switching to an equivalent flow rate of CO_2 or air. All runs were conducted until the weight loss was completed. The definition and calculation of the reactivity have been reported elsewhere [17].

DT coal was selected for three experiments: the first was designed to study the adsorption behavior of the organic contaminants in the AQ onto the surface of coal; the second was to investigate the effect of blending the AC on the combustion reactivity of DT; and the third was to investigate the co-processing performance of DT with the AQ and MS powder. Three sets of crucibles individually filled with 1.0 g of dried DT coal were used for the study. The first crucible set contained 1.0 g of dried DT coal only; the second set crucible contained 1.0 g of dried DT coal well mixed with 0.5 g of AQ and then dried at 105 °C for 2 h. The binary mixture prepared in this way was referred as to DT/AQ, and its increase in mass (m_i) should equal the mass of organic components adsorbed onto the coal particles (m_{oc}). A specific blending procedure was used for the third crucible set. In this experimental run, approximately 300 mg of MS powder was previously dissolved in 3 mL of AQ. Then, 0.5 g of the above solution containing dissolved MS was added to the crucible and mixed with coal. The mixture, denoted hereafter as DT/AQ-MS, was then dried at 105 °C for 2 h. The mass increase (m_i^*) included both the dissolved MS and the adsorbed organic components (m_{oc}^*) on the surface of the coal:

$$m_{oc}^* = m_i^* - (m_{a2} - m_{a1}) \tag{1}$$

where m_{a2} is the amount of ash in the DT/AQ-MS sample, and m_{a1} is the amount of ash in 1 g of DT coal.

Combustion tests of DT and its derivatives prepared as previously described (including DT/AQ and DT/AQ-MS) were performed in a muffle furnace at 850 °C under circulating air. The three sets of sample-filled crucibles were simultaneously placed into a muffle furnace and burned for different periods of time. The burn-off of coal samples after a period of combustion was calculated as follows:

$$\text{For the original DT coal : Burn-off (wt\%)} = \frac{w_1}{1 - m_{a1}} \times 100\% \tag{2}$$

$$\text{For DT/AQ coal : Burn-off (wt\%)} = \frac{w_2 - m_{oc}}{1 - m_{a1}} \times 100\% \tag{3}$$

$$\text{For DT/AQ-MS coal : Burn-off (wt\%)} = \frac{w_3 - m_{oc}^*}{1 - m_{a1}} \times 100\% \tag{4}$$

where w_1, w_2, and w_3 are the weight losses (g) after a period of combustion of DT, DT/AQ, and DT/AQ-MS, respectively.

2.4. Ash analyses

The chemical compositions of the coal ash were determined by inductively coupled plasma atomic emission spectroscopy and are reported as the percentage of the total weight for each metal elemental oxide.

The chemical forms of the mineral constituents in coal ashes were determined by X-ray diffraction analysis (XRD) on a Rigaku diffractometer (50 kV, 300 mA, Cu Kα radiation). The XRD pattern was analyzed with MDI Jade 5.0 software.

3. Results and discussion

3.1. Characteristics of coal and biomass samples

Table 1 gives ultimate and proximate analyses of the investigated coal and biomass samples. DL and DT are apparently similar in coal rank, ash content, and elemental composition. The chemical compositions of the coal ash samples are shown in Table 2. Significant differences in the mineral-phase chemical compositions of the DL and DT ashes were observed, particularly with respect to their CaO, SiO_2, and SO_3 contents. The CaO content in the DL ash was as high as 36.6 wt% but only 1.8 wt% in the DT ash. The SiO_2 content in the DT ash was ca. 54 wt%, which is nearly twice as large as that in DL ash (28.5 wt%). The differences in the sulfur contents reported in Tables 1 and 2 are notable. The results in Table 1 clearly indicate that the total sulfur in DL coal (0.2 wt%) was lower than that in DT coal (0.8 wt%), whereas the results in Table 2 show that the SO_3 content in the DL ash (7.9 wt%) was much higher than that in the DT ash (2.6 wt%). The related results will be further discussed in Section 3.5.

Table 2
Ash composition of coals.

Sample	Ash composition (wt%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
DL	28.5	11.6	10.3	36.6	1.6	7.9	1.6	0.6
DT	54.2	22.8	14.1	1.8	1.1	2.6	0.3	0.5
DT/AQ-MS	41.7	15.4	9.1	20.3	0.6	9.2	0.2	0.3

Table 1 also shows remarkable differences in the elemental compositions and chemical properties of the coal and biomass samples. The biomass materials contain less carbon, sulfur, and ash but substantially more oxygen and higher volatile matter than the coals; in addition, the biomass materials exhibit a lower calorific value (HHV). All of these shortcomings of biomass underscore its negative potential for being used as solid fuel.

3.2. Distribution and characterization of the products from biomass carbonization

In general, the carbonization of biomass produces three phases of products: solid biochar, condensable liquid, and non-condensable gases. Table 3 illustrates the yields of the solid and liquid products generated from the raw biomass samples at a carbonization temperature of 350 °C for 20 min. The biochar yields are in the range of 30–35 wt% (on biomass basis). The properties of the two biochar products presented in Table 1 differ substantially from those of their original feedstocks. Compared to the volatile content of the raw biomass (68–75 wt%), that of the biomass subjected to carbonization (21–23 wt%) decreased substantially. In contrast, the carbon content and the HHV of the biomass subjected to carbonization increased from *ca.*50 wt% to *ca.*75 wt% and from 18 to 20 MJ/kg to *ca.*28 MJ/kg, respectively. The high carbon content and caloric value of the biochar demonstrate its potential to be comparable to bituminous coals.

In the present study, the condensable liquid was fractionated into two sub-fractions: the HCO and AQ fractions. The HCO fraction was collected from a flask that was placed in an oil-bath thermostated at 110 °C. Therefore, this fraction should predominantly contain heavy organic components with boiling points greater than 110 °C. As shown in Table 3, the two HCO fractions derived from WS and BS, denoted as BS-HCO and WS-HCO, accounted for 21–23 wt% of the raw biomass. The proximate and elementary analyses of the BS-HCO fraction are given in Table 1. The results showed that BS-HCO was almost ash free and that both its carbon content (54.9 wt%) and HHV value (22.3 MJ/kg) were greater than those of the BS (49.4% and 18.4 MJ/kg, respectively). The caloric value of BS-HCO was even greater than that of the original biomass (18–20 MJ/kg). Additionally, as reported in Table 3, the bulk density of the two HCO fractions was in the range of 1.14–1.21 g/cm^3, which is substantially greater than that of the biochars (0.21–0.26 g/cm^3). These results clearly indicate the greater energy density of the HCO fraction, which should make this material easier to store, transport and use than fresh biomass feedstocks.

Table 3
Yields and properties of biochar and condensable liquids.

Property	Biochar		Condensable liquids			
	WS-350	BS-350	WS-HCO[a]	BS-HCO[a]	WS-AQ[b]	BS-AQ[b]
Yield[c](wt%)	34.6	30.4	20.7	23.3	17.8	20.8
Density (g/cm^3)	0.2122	0.2557	1.1357	1.2084	1.0589	1.0162
Water (wt%)	–	–	14.1[d]	13.6[d]	78.9[e]	80.3[e]
pH[f]	–	–	–	–	2.1	2.4

[a] Heavy condensable oil.
[b] Aqueous condensate.
[c] Dry biomass basis.
[d] HCO basis.
[e] AQ basis.
[f] Measured at room temperature.

Particular attention was paid to the AQ fraction, which was obtained by further cooling the distilled vapor from the flask warmed at 110 °C. As evident from the results summarized in Table 3, the yield of the AQ fractions ranged from 17.8 to 20.8 wt%, which is lower than that of the HCO fractions. The water content in the AQ fractions was as high as *ca.* 80 wt%. From the point of view of using these materials as fuels, this fraction has less potential for direct energy uses. The water produced resulted from original moisture in the feedstock and from dehydration reactions during carbonization of the biomass [18]. All organic compounds in this fraction should have a boiling point less than 110 °C. In this research, only the BS-AQ was subjected to compositional analysis by gas chromatography–mass spectrometry. Well-identified compounds in the BS-AQ are summarized in Table 4. As evident from the results in the table, chemicals of numerous groups were observed, including carboxylic acids, alcohols, phenols, ketones, and aldehydes. Among these compounds, acetic acid was the most abundant component. The presence of such acidic components in the AQ fraction results in its substantial acidity, it exhibits a pH value between 2.1 and 2.4 (see Table 3). In addition to the chemical compounds listed in Table 4, numerous un-identified and undetectable substances were present, such as phenolic derivatives and light tars that co-exist in the AQ. Most of these substances are toxic and carcinogenic, and the arbitrary discharge of the AQ will cause serious environmental pollution, offsetting the advantages of biomass pre-treatment via torrefaction or carbonization.

3.3. Adsorption behavior of the organic contaminants during the blending of coal and AQ

In view of the previously discussed disadvantages of the AQ, we attempted to combine coal gasification or combustion with simultaneous disposal of the AQ. For this purpose, coal was preliminarily blended with the AQ and then co-gasified or co-combusted. During the blending operation, the organic contaminants in the AQ could be physically or chemically adsorbed onto coal particles. In addition, some acidic volatiles, such as acetic acid can react with mineral matter in coal to form thermally stable compounds in the following manner:

$$CaCO_3 + 2CH_3COOH = Ca(CH_3COO)_2 + H_2O + CO_2 \uparrow \tag{5}$$

In the blending test run, 1.0 g of DT coal was blended with 0.5 mL of either WS-AQ for the preparation of DT/AQ or its solution containing dissolved MS for the preparation of DT/AQ-MS. The mixtures were dried at 105 °C for 2 h for later use. For comparison, 0.5 mL of WS-AQ was dropped into a glass dish and evaporated under the same conditions. The mass values of the organic adsorbate on DT/AQ and DT/AQ-MS were determined by mass balance, as described in the Experimental Section 2.3. Fig. 1 compares the mass values of the organic adsorbate on DT/AQ (m_{oc}) and DT/AQ-MS (m^*_{oc}), along with the residual mass (m_{re}) of 0.5 mL of the AQ after evaporation at 105 °C. The mass of adsorbate on the DT/AQ-MS ($m^*_{oc} = 80.5$ mg) was greater than that on the DT/AQ ($m_{oc} = 66.1$ mg); both were twice the mass of the evaporation residuals of the AQ ($m_{re} = 27.8$ mg). These results suggest that some organic volatiles were strongly bonded with the functional sites on coal or reacted with mineral matter to form more stable compounds during the blending operation. According to the density and water content data in Table 3, we estimated that 0.5 mL of WS-AQ contained approximately 111.7 mg of organic matter. Accordingly, the data in Fig. 1 revealed that the organic adsorbates on DT/AQ and DT/AQ-MS accounted for 60–70% of all the organic components in the AQ, corresponding to a biomass adsorbate to coal mass ratio of 7–8:100.

Table 4
Chemical composition of BS-AQ.

Composition (wt%)	BS-AQ
Water	80.3
Acetic acid	7.9
Acetol	2.0
Methanol	1.3
Propionic acid	0.79
1-Hydroxy-2-butanone	0.77
Methyl acetate	0.45
Phenol isomers	0.43
Cyclopentenone isomers	0.29
2.2-Furaldehyde	0.24
γ-Buthyrolacton	0.2
2-Methoxyphenole	0.17
Furfural	0.13
2(3*H*) Furanone	0.1
Acetone	0.04
Other organics (Diff.)	4.89

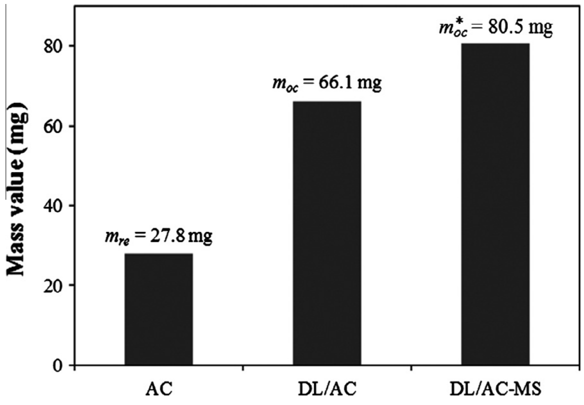

Fig. 1. The mass values of the residuals from AQ and the organic adsorbates on DT/AQ and DT/AQ-MS after evaporation or drying at 105 °C for 2 h.

3.4. Synergistic effects of co-processing calcium-rich coal with AQ

Fig. 2 shows typical gasification profiles of DL (Fig. 2a) char and its AQ-blended chars (Figs. 2b and c) in CO_2 at 850 °C. In this experimental run, DL coal was mixed with AQ in different ratios. The binary mixture (denoted as DL/AQ) was dried and then pyrolyzed in a muffle furnace. Interestingly, the gasification reactivity of DL/AQ chars increased with increasing AQ dosage. When DL and AQ were mixed in a mass ratio of 1:1 (Fig. 2c), the gasification reactivity at $x = 0.5$ of the produced char (0.024 min^{-1}) was nearly twice that of the raw DL char (0.013 min^{-1}). Fig. 2 also gives their combustion reactivity profiles in air at 800 °C. Again, the reactivity of the DL/AQ char (Fig. 2e) was definitely enhanced in comparison with that of the raw DL char (Fig. 2d).

The ability of AQ to quicken char gasification and combustion when added to DL coal warranted further investigation. A satisfactory explanation can be provided through investigation and comparison of some of the relevant characteristics of DL, AQ, and their mixtures. Two noteworthy points related to DL are set forth in Table 2 and Fig. 3. The results in Table 2 indicate that DL coal is extremely abundant in calcium, and the XRD pattern of DL coal in Fig. 3 (pattern *a*) indicates strong diffractions assigned to calcite (PDF No. 47-1743), thereby suggesting that poorly dispersed calcite with particle sizes larger than 5 nm [19,20] are present in the DL coal. However, great differences were observed between the XRD patterns of the DL coal and that of its AQ-mixed samples. As can be seen from Fig. 3, the intensities of the calcite diffraction peaks become weak and entirely disappear at 4:1 (pattern *b*) and 1:1 (pattern *c*) DL to AQ mass ratios, respectively. This result is closely associated with the chemical compositions of the AQ fractions, as reported in Tables 3 and 4. Table 3 shows that the AQ fractions are highly acidic, with pH values between 2.1 and 2.4. Table 4 illustrates that the acidity of the AQ is attributable to the presence of various organic components, particularly acetic acid. Collectively, these analytical results offer a satisfactory explanation for the ability of AQ to quicken char gasification and combustion when added to DL coal; i.e., the indigenous crystalline calcite mineral in DL coal is poorly dispersed, and it exhibits lower catalytic activity than when highly-dispersed. When DL coal is mixed with the AQ, various organic acidic components in the AQ may partially or absolutely dissolve and redistribute the crystalline calcite in DL coal, which results in many more crystalline calcium species being highly dispersed on the surface of coal as an in-situ catalyst, which, in turn, results in enhanced reactivity of the chars during gasification or combustion. This synergistic effect is one of the most attractive benefits of co-processing calcium-rich coal with AQ.

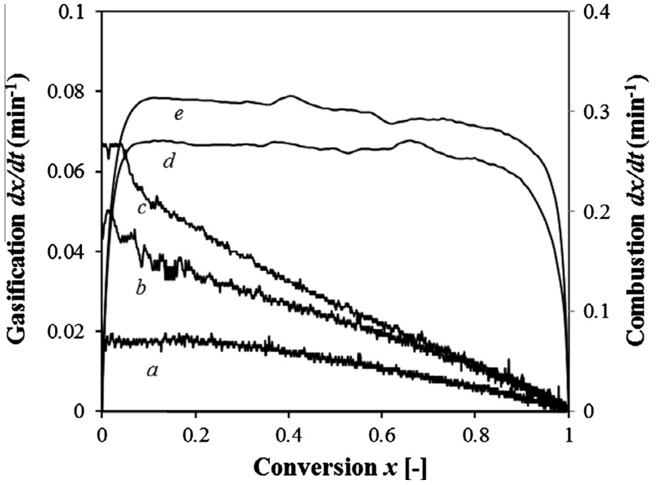

Fig. 2. CO_2 gasification (at 850 °C) and combustion (at 800 °C) of DL-related chars: (a) and (d) DL char; (b) DL/AQ char (4:1); (c) and (e) DL/AQ char (1:1).

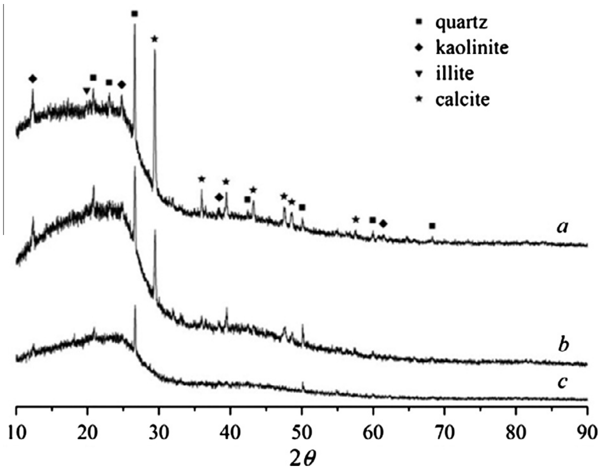

Fig. 3. XRD profiles of (a) DL coal, (b) a 4:1DL/AQ mixture and (c) a 1:1DL/AQ mixture.

In this study, DL and DT coals were chosen for their similar coal ranks and remarkable differences in calcium contents. First, we compared the data for CO_2 gasification reactivity of raw DL and DT chars, as determined by thermogravimetric analysis. The results are illustrated in Fig. 4. We observed that the gasification reactivity of the DL char was almost ten times greater than that of the DT char. This remarkable difference can be attributed to the fact that the amount of mineral-phase calcium in the DL coal was much higher than that in DT coal, as indicated in Table 2. Among the mineral constituents of coal, calcium has been well established to exert a maximum catalytic effect on char reactivity, which explains why the DL char exhibited greater reactivity than the DT char.

In view of the catalytic and synergistic effects of calcium during the co-processing of DL coal and AQ, we attempted to improve the reactivity of DT coal using a novel calcium loading procedure, where MS was previously dissolved in WS-AQ and then mixed with DT coal. MS is one of the most common types of seashells that consist predominantly of calcium carbonate. Previous studies have revealed that the particle form of calcium species is shown to have no or little catalytic activity for char gasification [19–21]. This means that there would be no catalytic and synergistic effects when just co-processing MS and coal directly. The procedure of pre-dissolving MS in WS-AQ is expected to enable the dissolved calcium being highly dispersed on the surface of DT coal for use

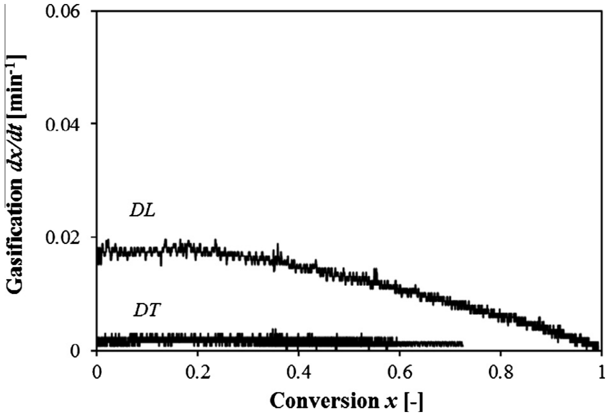

Fig. 4. CO_2 gasification profiles of DL and DT chars at 850 °C.

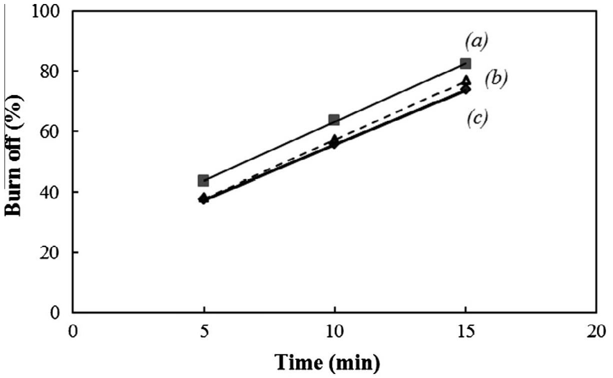

Fig. 5. Burn-off of (a) DT/AQ-MS, (b) DT/AQ, and (c) DT coals as a function of burning time at 850 °C.

as a catalyst support, which in turn promotes coal gasification and combustion reactions. As shown in Table 2, this operation increased the content of calcium oxide from 1.8 wt% in raw DT ash to 20.3 wt% in DT/AQ-MS ash. Fig. 5 shows the combustion results for DT, DT/AQ, and DT/AQ-MS in a muffle furnace. In the case of DT/AQ and DT/AQ-MS, the contribution of the adsorbate on the surface of the coal to the burn-off has been subtracted as indicated in Eqs. (3) and (4). No evident change in the burn-off between DT and DT/AQ was observed, which suggests that the blending of AQ scarcely influenced the combustion reactivity of DT. On the other hand, an obvious and reproducible improvement in the burn-off for DT/AQ-MS was observed, which provided a potential way of co-processing calcium-deficient coal with shell wastes and AQ.

3.5. In-situ desulfurization performance of mineral-phase calcium

The chemical forms of the mineral constituents in coal ashes were investigated by XRD analysis. Fig. 6 shows XRD patterns of three typical ash samples produced from DL, DT, and DT/AQ-MS. The mineral matter of the DL ash (pattern a) comprised quartz (PDF No. 65-0466), lime (PDF No. 48-1467), anhydrite (PDF No. 37-1496) and hematite (PDF No. 33-0664), whereas the XRD pattern of DT ash (pattern c) primarily showed diffraction peaks assigned to quartz and hematite. No peaks assigned to calcium species were observed. The difference in the XRD pattern between DL and DT ashes was mainly attributed to their different calcium contents. However, the XRD patterns for the DT/AQ-MS ash exhibited strong diffractions from anhydrite (pattern b), suggesting that the vast majority of the loaded calcium was contributed to the capture of sulfur during DT/AQ-MS combustion. This hypothesis was supported by the data shown in Table 2, where the SO_3 content in the DT/AQ-MS ash (9.2 wt%) was greater than that in the DT ash (2.6 wt%). The results provide evidence that the use of either calcium-rich coal or calcium-deficient coal activated by shell wastes and AQ is helpful to achieving in-situ desulfurization.

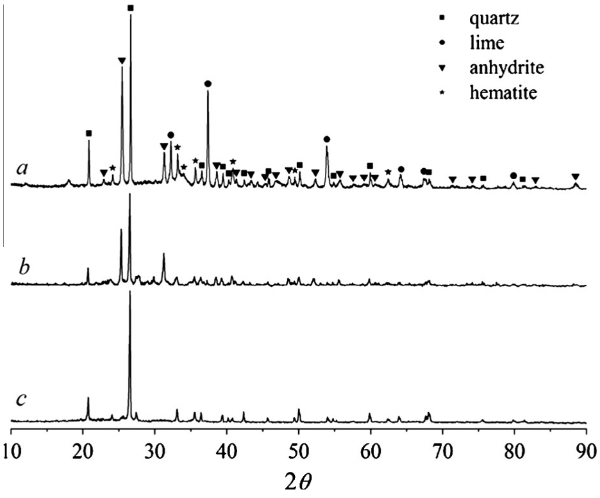

Fig. 6. XRD profiles of (a) DL, (b) DT/AQ-MS and (c) DT ashes.

4. Conclusions

Biomass carbonization produced two energy-enriched products—biochar and HCO, along with a water-rich AQ fraction containing small amounts of organic contaminants. A combined approach to co-processing calcium-rich coal and AQ was explored. The technical benefits of this approach include: (1) about 60–70% of all the organic contaminants in the AQ were strongly bonded with the functional sites on coal or reacted with mineral matter to form more stable compounds during the blending of AQ and coals, corresponding to a biomass adsorbate to coal mass ratio of 7–8:100; (2) when mixing AQ with a calcium-rich DL coal in a mass ratio of 1:1, the CO_2 gasification (at 850 °C) and combustion (at 800 °C) reactivities at $x = 0.5$ of the produced char were nearly twice and 1.2 times those of the raw DL char, respectively; (3) when co-processing a calcium-deficient DT coal with shell wastes and AQ, an obvious and reproducible improvement in the burn-off for DT/AQ-MS was observed; and (4) the XRD analysis provided evidence that the use of either calcium-rich coal or calcium-deficient coal activated by shell wastes and AQ is helpful to achieving in-situ desulfurization.

There were no direct data to assess the economic feasibility of the approach proposed in this study. However, the catalytic and synergistic effects observed when co-processing calcium-rich coal with AQ would certainly be beneficial to increase the throughput of a given gasifier or boiler. On the other hand, AQ is a wastewater fraction originating from the upgrading of biomass via torrefaction or low-temperature carbonization. The treatment of AQ by means of traditional technologies is energy intensive and costly. In this sense, the disposal of AQ in combination with gasification or combustion of calcium-rich coal provides a practical and feasible means that can reduce specific disposing costs to allow better use of AQ than would be the case of just disposing it in conventional wastewater treatment processes.

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